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Indian Standard

METHODS OF SAMPLING AND TEST FOR
NATURAL AND SYNTHETIC PERFUMERY
MATERIALS

PART IX DETERMINATION OF ESTER VALUE AFTER
ACETYLATION AND FREE ALCOHOLS

(*Second Revision*)

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Indian Standard**METHODS OF SAMPLING AND TEST FOR
NATURAL AND SYNTHETIC PERFUMERY
MATERIALS****PART IX DETERMINATION OF ESTER VALUE AFTER
ACETYLATION AND FREE ALCOHOLS****(Second Revision)**

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Indian Standard
**METHODS OF SAMPLING AND TEST FOR
NATURAL AND SYNTHETIC PERFUMERY
MATERIALS**

**PART IX DETERMINATION OF ESTER VALE AFTER
ACETYLATION AND FREE ALCOHOLS**

(*Second Revision*)

0. FOREWORD

0.1 This Indian Standard (Part IX) (Second Revision) was adopted by the Indian Standards Institution on 25 January 1980, after the draft finalized by the Natural and Synthetic Perfumery Materials Sectional Committee had been approved by the Petroleum, Coal and Related Products Division Council.

0.2 This standard was first published in 1952 entitled as 'Methods of test for essential oils' and subsequently revised in 1968 as 'Methods of sampling and test for natural and synthetic perfumery materials'. Taking cognizance of the need to incorporate instrumental methods of analysis now in vogue and to facilitate inclusion of additional test methods or changes in the existing test methods and also to align these test methods with the corresponding ISO Standards, the Committee concerned decided to revise and split the standard and publish individual test methods as separate parts of the original standard.

0.2.1 In order to facilitate proper referencing of the method of test given in this revised part of IS : 326, Amendment No. 2 is being issued separately to the relevant clause of IS : 326-1968* which would no longer be in force with the publication of this revision. The test method as given in this revised part will supersede the test method as given under 11 of IS : 326-1968*.

0.3 In the preparation of this standard, assistance has been derived from the following publications:

ISO/R 1241-1971 Essential oils — Estimation of free alcohols content by determination of ester value after acetylation. International Organization for Standardization.

* Methods of sampling and test for natural and synthetic perfumery materials (first revision).

BS 2703 : 1976 Methods of test for essential oils. British Standards Institution.

0.4 In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS : 2-1960*.

1. SCOPE

1.1 This standard (Part IX) prescribes two methods, namely, (a) acetic anhydride method, (b) dimethylaniline/acetyl chloride method, for the determination of ester value after acetylation of natural and synthetic perfumery materials. The content of free alcohols is determined by calculation.

2. TERMINOLOGY

2.1 For the purpose of this standard, the definitions given in IS : 6597-1972† and the following shall apply.

2.1.1 *Ester Value After Acetylation* — The number of milligrams of potassium hydroxide required to neutralize the acid liberated by the hydrolysis of 1 g of the acetylated perfumery material.

3. DETERMINATION OF ESTER VALUE AFTER ACETYLATION AND FREE ALCOHOLS

3.1 Method A — Acetic Anhydride Method

3.1.0 *Outline of the Method* — The perfumery material is acetylated by acetic anhydride in the presence of sodium acetate followed by alkaline hydrolysis. Excess alkali is titrated to determine the ester value after acetylation.

NOTE 1 — This method is not suitable either for perfumery materials containing appreciable quantities of tertiary alcohols (linalol and terpineol the acetylation of which would be incomplete) or for perfumery materials containing appreciable quantities of phenols, lactones, aldehydes or enolysable ketones, which could be acetylated at the same time as the perfumery material.

NOTE 2 — In certain materials, like citronella oil, the results shall be expressed as total acetylizible matter calculated as the major alcohol.

3.1.1 Apparatus

3.1.1.1 *Acetylation flask* — 100 ml capacity, round-bottomed acetylation flask with a ground-glass neck, provided with a glass tube at least 1 m in length and about 10 mm internal diameter to act as a reflux condenser.

*Rules for rounding off numerical values (revised).

†Glossary of terms relating to natural and synthetic perfumery materials.

3.1.1.2 Saponification flask — 100 to 250 ml capacity, consisting of an alkali resistant glass flask, with ground-glass neck, a ground-glass tube at least 1 m in length and about 10 mm internal diameter.

3.1.2 Reagents

3.1.2.1 Acetic anhydride — See IS : 1235-1958*.

3.1.2.2 Sodium acetate — anhydrous, freshly fused and powdered.

3.1.2.3 Sodium carbonate — 2 percent preferably in brine.

3.1.2.4 Sodium chloride solution — saturated aqueous solution.

3.1.2.5 Magnesium sulphate or sodium sulphate — anhydrous, neutral, freshly ignited.

3.1.2.6 Potassium hydroxide solution — 0.1 N solution in 95 percent ethanol (v/v).

3.1.2.7 Hydrochloric acid — 0.5 N.

3.1.3 Procedure — Mix approximately 10 ml of the sample of perfumery material, 10 ml of acetic anhydride and 2 g of anhydrous sodium acetate in the acetylation flask. Add fragments of pumice-stone or porcelain and fit the flask with its reflux condenser.

Heat the flask by means of any suitable heating device and gently reflux the liquid for 2 hours.

At the end of this period, allow the liquid to cool; add 50 ml of water and heat at a temperature between 40 and 50°C for 15 minutes with shaking frequently. Cool to room temperature, remove the reflux tube and transfer the liquid to a separating funnel; wash the flask twice with 10 ml of water and add these washings to the contents of the separating funnel. Wait until separation of the liquid is complete, then reject the aqueous layer.

Wash the oil layer by shaking successively with:

- a) 50 ml of sodium chloride solution (3.1.2.4),
- b) 50 ml of sodium carbonate (3.1.2.3),
- c) 50 ml of sodium chloride solution (3.1.2.4), and
- d) 20 ml of water.

Shake the acetylated perfumery material vigorously with the saturated solutions, and gently with water which, if the washings have been properly conducted, will be neutral to litmus paper.

Run the acetylated material into a dry tube and shake intermittently several times with about 2 to 3 g of anhydrous magnesium sulphate or

*Specification for acetic anhydride.

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anhydrous sodium sulphate till it is dried. Filter the dried material through dried filter paper in a covered funnel.

In the saponification flask, weigh, to the nearest 0.5 mg, about 2 g of the acetylated perfumery material, and add 2 ml of water and 0.5 ml of phenolphthalein indicator.

Neutralize the liquid with the ethanolic potassium hydroxide solution (3.1.2.6) using the burette.

Determine the ester value following the procedure given in IS: 326 (Part VIII)-1980*, but adding 25 ml of 0.5 N ethanolic potassium hydroxide solution depending upon the mass of the sample taken.

3.1.3.1 Blank determination — Simultaneously with the hydrolysis of the acetylated material by the procedure prescribed in IS: 326 (Part VIII)-1980*, carry out a blank determination of the ethanolic potassium hydroxide by the same procedure but omitting the perfumery material.

3.1.4 Calculation

$$3.1.4.1 \text{ Ester value after acetylation} = \frac{56.1 \times N \times (V_1 - V_2)}{m}$$

where

V_1 = volume in ml of hydrochloric acid required for the blank,

V_2 = volume in ml of hydrochloric acid required to neutralise the excess alkali after hydrolysis,

N = normality of hydrochloric acid used for titration, and

m = mass in g of acetylated material.

Express the result to the first decimal place and state which of the two methods of acetylation has been used.

NOTE — In this, it is assumed that the alcohols are monohydric and the acids monobasic.

$$3.1.4.2 \text{ Content of free alcohols (uncombined), percent by mass} = \frac{M \times (E_1 - E_2)}{561 - 0.42 E_1}$$

where

E_1 = ester value of the material after acetylation,

E_2 = ester value of the material before acetylation, and

M = molecular mass of the specified alcohol.

*Methods of sampling and test for natural and synthetic perfumery materials: Part VIII Determination of ester value, content of esters and combined alcohols (second revision).

3.2 Method B — Dimethylaniline Acetylchloride Method (Fiore Method)

3.2.0 Outline of the Method — The perfumery material is acetylated by acetyl chloride in the presence of dimethylaniline and acetic anhydride followed by alkaline hydrolysis. Excess alkali is titrated to determine the ester value after acetylation.

NOTE — This method is applicable for tertiary alcohols, namely, linalol and terpineol excluding cedrol.

3.2.1 Apparatus

3.2.1.1 Saponification flask — same as in 3.1.1.2.

3.2.1.2 Graduated measuring cylinders — unstoppered, 50 ml graduated in 1 ml and stoppered, 10 ml graduated in 0.2 ml (see IS : 878-1975*).

3.2.1.3 Burette — 25 ml capacity, graduated in 0.1 ml (see IS : 1997-1967†).

3.2.2 Reagents

3.2.2.1 Dimethylaniline — freshly distilled and free from methylaniline and aniline.

3.2.2.2 Acetic anhydride — See IS : 1235-1958‡.

3.2.2.3 Acetyl chloride

3.2.2.4 Sodium sulphate solution — 10 percent (m/v).

3.2.2.5 Sulphuric acid — 2.5 percent (m/v).

3.2.2.6 Sodium bicarbonate solution — 50 percent (m/v).

3.2.2.7 Magnesium sulphate — anhydrous, neutral, freshly ignited and powdered.

3.2.2.8 Potassium hydroxide solution — 0.1 N and 0.5 N solution in 95 percent ethanol (v/v).

3.2.2.9 Hydrochloric acid — 0.5 N.

3.2.2.10 Phenolphthalein indicator solution — Dissolve 0.2 g phenolphthalein in 100 ml of 95 percent ethanol.

3.2.3 Procedure — Introduce 10 ml of the sample of perfumery material into the 100-ml glass-stoppered conical flask. Add 20 ml of dimethylaniline. Stopper the flask and mix thoroughly. Cool in melting ice and add 8 ml of acetyl chloride followed by 5 ml of acetic anhydride. Keep the flask in the ice-bath throughout the addition and allow it to stand at room temperature for 30 minutes. Immerse the flask for 16 hours in the water-bath maintained at $40 \pm 1^\circ\text{C}$. Cool to room temperature,

*Specification for graduated measuring cylinders (first revision).

†Specification for burettes (first revision).

‡Specification for acetic anhydride.

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transfer the contents of the flask to the separating funnel and wash by shaking successively with:

- a) Twice with 75 ml of sodium sulphate solution,
- b) Five times at least with 50 ml of sulphuric acid until the washings are free from dimethyl aniline as demonstrated by freedom from turbidity when the last washing is made alkaline.
- c) Twice with 25 ml of sodium bicarbonate solution, and
- d) Twice with 25 ml of sodium sulphate solution.

Shake vigorously for 30 seconds with each solution and allow to separate. Check the neutrality of the last solution to litmus paper.

Dry the acetylated material with 2 g to 3 g of magnesium sulphate for at least 2 hours with intermittent shaking. Then, filter the material through a dry filter paper in a covered funnel.

Add 2 ml of water and 2 ml of phenolphthalein indicator solution. Neutralize the free acidity with potassium hydroxide solution using the burette. Not more than one drop should be required to give a pink colour. Take the first pink colour as the neutral point as certain esters, namely, linalyl acetate are easily hydrolyzed.

Determine the ester value of the acetylated material by the procedure as given in IS : 326 (Part VIII)-1980.*

NOTE — In certain perfumery materials where the principal tertiary alcohol is linalol, boil (hydrolyze) with ethanolic potassium hydroxide solution for one hour where the principal tertiary alcohol is terpineol, boil for 2.5 hours.

3.2.3.1 Blank determination — Simultaneously with the hydrolysis of the acetylated material by the procedure as prescribed in IS : 326 (Part VIII)-1980*. Carry out a blank determination on the ethanolic potassium hydroxide by the same procedure but omitting the acetylated material.

3.2.4 Calculation — Calculate the ester value after acetylation using the formula given under 3.1.4.

*Methods of sampling and test for natural and synthetic perfumery materials: Part VIII Determination of ester value, content of esters and combined alcohols (second revision).